

Proceeding Paper

Electrical Conductivity and Nyquist Plot of $C_4C_1Im\ BF_4$ at Room Temperature by Impedance Spectroscopy [†]

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[†] Presented at the 24th International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2020; Available online: <https://ecsoc-24.sciforum.net/>.

Abstract: Ionic liquids (ILs) represent a real alternative for electrochemical applications due to their remarkable characteristics, namely a very low vapour pressure, low flammability, high thermal stability, wide potential window and high ionic conductivity. In this work, Nyquist plot and impedance spectroscopy at room temperature is proposed as an alternative method to obtain the ionic conductivity for ionic liquids by using an Agilent HP 4284A RLC precision meter. For this propose, the IL 1-butyl-3-methylimidazolium tetrafluoroborate ($C_4C_1Im\ BF_4$) was selected and results were compared with the previously obtained from the conductimeter CRISON GLP31.

Keywords: ionic liquid; dielectric spectroscopy; electrolytes; impedance

Citation: Vallet, P.; Parajó, J.J.; Sotuela, F.; Morcillo, A.; Villanueva, M.; Cabeza, O.; Varela, L.M.; Salgado, J. Electrical Conductivity and Nyquist Plot of $C_4C_1Im\ BF_4$ at Room Temperature by Impedance Spectroscopy. *Chem. Proc.* **2021**, *3*, 119. <https://doi.org/10.3390/ecsoc-24-08369>

Academic Editors: Julio A. Seijas and M. Pilar Vázquez-Tato

Published: 14 November 2020

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1. Introduction

Ionic liquids (ILs) are salts designed by a combination of an organic cation and an inorganic/organic anion with a melting point below 100 °C [1]. ILs with the melting point below room temperature are known as room-temperature ionic liquid (RTILs). Taking into account the big amount of possible anions and cations [2], the number of possible ILs becomes very big. Thus, Earle and Seddon [3] have estimated the number of RTILs with different combinations at near one billion, which is why ILs are referred to as tuneable liquids that can be chosen for each application.

One of the pioneers in the study of ionic liquids was Walden, who in the 1910s synthesized and studied the first ionic liquid, ethylammonium nitrate, and over the time some interesting properties of this first IL have been reported and it is even still under study nowadays. In the upcoming decades, interest in ILs is expected to become significant with thousands of studies of their properties, features, synthesis, etc. [4]. Currently, ILs can be considered as a referent in electrochemistry [5] and many other fields [6]. One of the most studied IL is $C_4C_1Im\ BF_4$, thermophysical, thermodynamics [7] and electrochemical properties like conductivity [8] among others are fully reported in the literature.

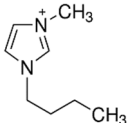
The most interesting property analysed in electrochemical applications is the ionic conductivity as indicated by the numerous studies on the subject [3,4,8–11]. Therefore, it is important to characterise in depth this property. In this work, impedance spectroscopy methodology is used to determine the ionic conductivity of the IL $C_4C_1Im\ BF_4$. Results obtained are compared with the ones obtained using a conductimeter.

2. Materials and Methods

Chemicals

The name, molecular weight, chemical structure, abbreviation, CAS number and provenance of the chemical compound used in this work can be found on Table 1. The sample was kept under sealed vacuum for 48 h.

Table 1. Chemicals.

Name	Molecular Weight (g·mol ⁻¹)	Structure	Abbreviation CAS Number	Provenance
1-Butyl-3-methylimidazolium tetrafluoroborate	226.02	 BF ₄ ⁻	C ₄ C ₁ Im BF ₄ 174501-65-6	ACROS ORGANICS

3. Experimental

3.1. LCR Precision Meter

In order to obtain an impedance spectroscopy curve, a HP 4284A RLC precision meter from Agilent (Santa Clara, CA, USA) was used in the frequency range of 20 Hz to 1 MHz over 8610 selectable frequencies. The RLC presents 6 digit resolution at any range, and a basic accuracy of 0.05%. 20 impedance parameters can be measured, and the measurement range depends on the selected parameter, i.e., G and B (admittance and conductance used in this work to obtain the dielectric spectroscopy) present a range from 0.01 nS to 99.9999 S, and Z' and Z'' (real and imaginary part of the impedance, or resistance and reactance respectively, used for the Nyquist plot determination) present a range from 0.01 mΩ to 99.9999 Ω [12]. The sample was placed into a Swagelok sealed coin cell with two parallel plate electrodes of stainless steel with 1 mm thickness and 8 mm diameter.

3.2. Electrical Conductivity

The electrical conductivity obtained by impedance spectroscopy was compared with the value obtained by the a GLP31 conductimeter (CRISON, Barcelona, Spain) which presents a conductivity range from 0.01 μS/cm to 500 mS/cm. The accuracy of the conductimeter is ≤0.5% in conductivity measurement. The conductimeter was previously calibrated before the measurement with standard solutions at a 298 K. The probe is formed by two parallel electrodes of platinum which can take measurements in a temperature range from 243 to 323 K.

3.3. Temperature Stabilization

A calibrated F25 thermostat (Julabo, Peterborough, UK) was used to control the temperature of the sample; the error in the temperature was lower than 0.1 K. These measurements need to be taken in an isothermal regime, so the time spent in every measurement was, at least 15 min.

4. Methodology

The admittance of a conductive sample can be defined as:

$$Y = \frac{1}{Z} = G + jB \quad (1)$$

where Z is the impedance, G the conductance, B the susceptance and j the imaginary number. The conductance and the susceptance can be related with the capacity of the sample (C) and the dissipation factor (D) by the following mathematic relations:

$$B = 2\pi fC \quad (2)$$

$$D = \frac{G}{|B|} \quad (3)$$

The complex dielectric constant is defined as:

$$\varepsilon = \varepsilon' + j\varepsilon'' \quad (4)$$

where ε' and ε'' are the real and imaginary parts, respectively, of the dielectric constant. If the sample is placed in an electric capacitor, the real and the imaginary part of the sample can be obtained as:

$$\varepsilon' = \frac{C}{C_0} \quad (5)$$

$$\varepsilon'' = \frac{C \cdot D}{C_0} \quad (6)$$

where C_0 is vacuum capacitance, defined as:

$$C_0 = \varepsilon_0 \frac{A}{h} \quad (7)$$

where ε_0 is the vacuum dielectric constant, A the cross-sectional area of the capacitor and h the width of the sample. The conductive regime of the sample is given by the linear part of ε'' , this linear regime can be described by pure Ohmic conduction by the following model:

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} \quad (8)$$

where σ is the conductivity and ω the angular frequency. For data analysis the region where the slope is -1.00 ± 0.02 on $\log \varepsilon''$ vs. $\log \omega$ representation, was selected, and the conductivity can be obtained by two methods, a linear fitting of the parameters and by averaging of the conductivity of the every value in the conductive regime of the sample.

5. Results

Figure 1A shows the conductance (G) and the susceptance (B) obtained directly from RLC of the C_4C_1 Im BF_4 . By applying equations (2) and (3), it is possible to obtain the capacitance (C) and the dissipation factor (D), which are presented in Figure 1B,C, respectively.

The complex dielectric constant (Figure 2A) can be obtained by application of Equations (5) and (6) and considering the vacuum capacitance (C_0) of the coin cell used. As it can be seen, the linear region of the imaginary part of the dielectric constant of this IL begins around 10^4 Hz. Figure 2B shows the logarithm of ε'' vs. the logarithm of the angular frequency (ω), which corresponds to the conductive regime of this IL. This spectroscopic window fits well to the following linear equation:

$$\ln \varepsilon'' = 24.031 - 0.983 \cdot \ln \omega \quad (9)$$

From the fitting parameters, the conductivity of this IL can be obtained by application of Equation (8):

$$\sigma = 8.8542 \times 10^{-12} \cdot \text{Exp}[24.031] = 0.242 \text{ S/m} \quad (10)$$

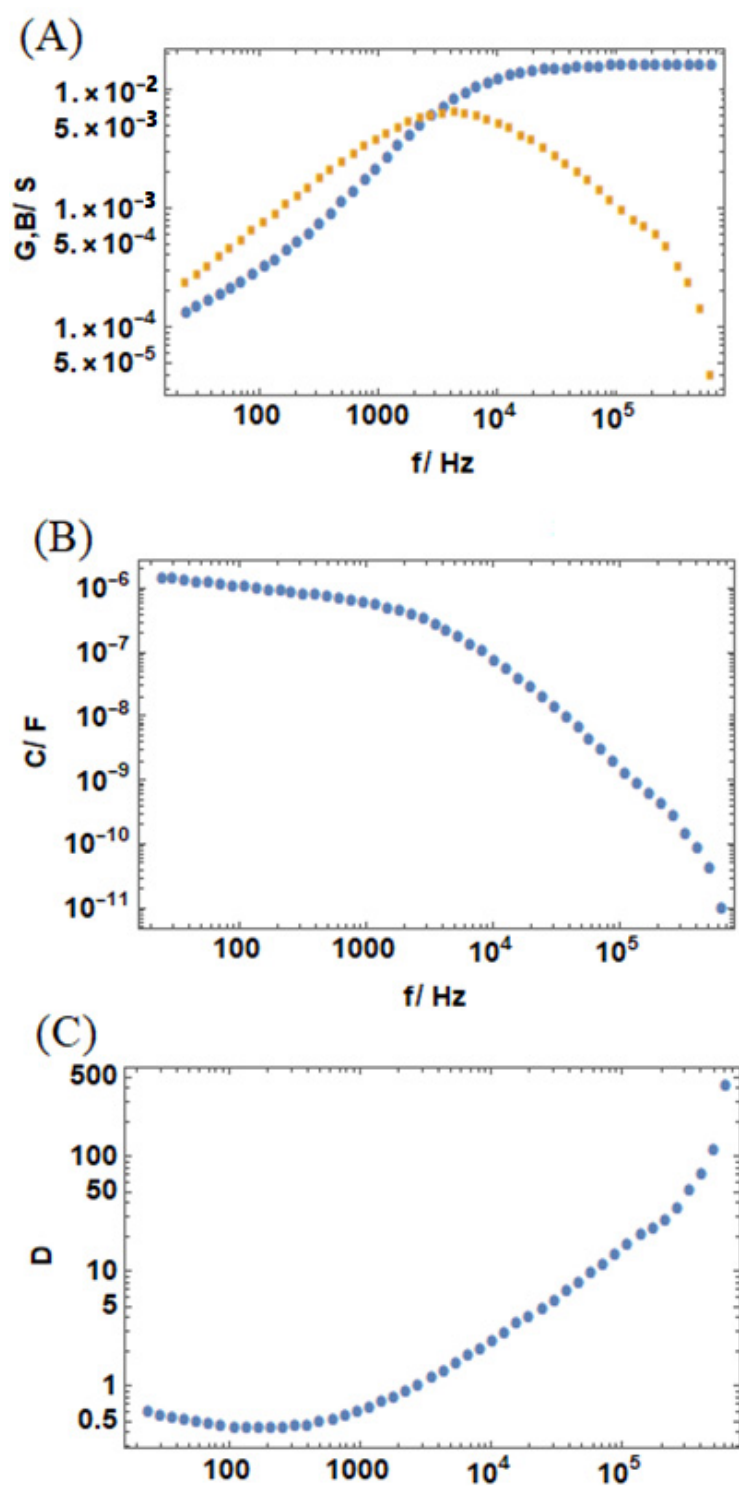


Figure 1. (A) Conductance (blue dots) and susceptance (orange square) of $C_4ClIm BF_4$. (B) Capacitance of the sample. (C) Dissipation factor.

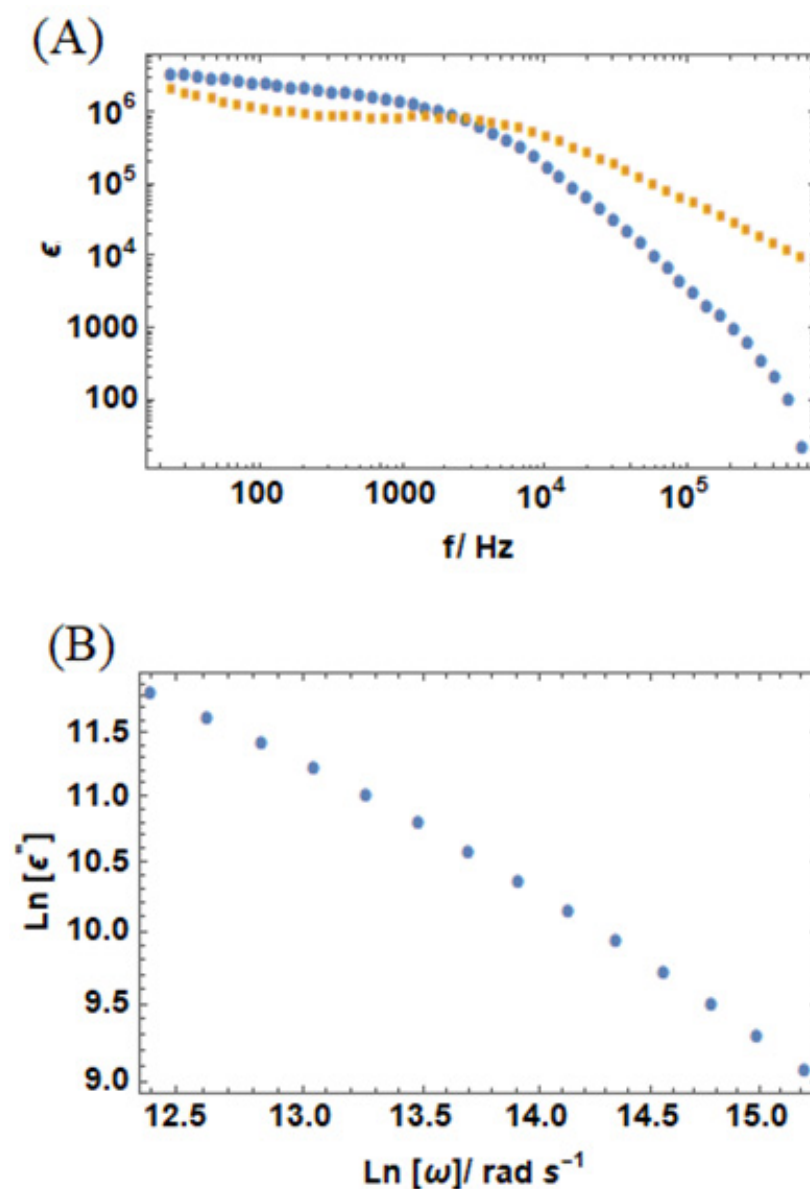


Figure 2. (A) Real part of complex dielectric constant (blue dots), and imaginary part of the complex dielectric constant (orange squares). (B) Linear region (conductive regime) of the imaginary part of the dielectric constant.

Furthermore, the conductivity can be obtained by averaging of the conductivity values in the conductive regime of IL. Figure 3 shows the conductivity vs. frequency (obtained from Equation (8)), where it is clearly seen that the conductive regime begins around 10^4 Hz, as mentioned above. As previously pointed out, the average value of conductivity on conductive regime is 0.28 ± 0.09 S/m.

Figure 4 shows the Nyquist plot (Z' vs. Z'' , this plot is a frequency response plot used to assess the stability of a system with feedback) of the $C_4C_1Im BF_4$ at room temperature. It can be clearly seen that the frequency range is not enough to observe the full semicircle of the dielectric relaxation, so unfortunately, the spectroscopic frequency window used in this system is not the suitable to study this phenomenon.

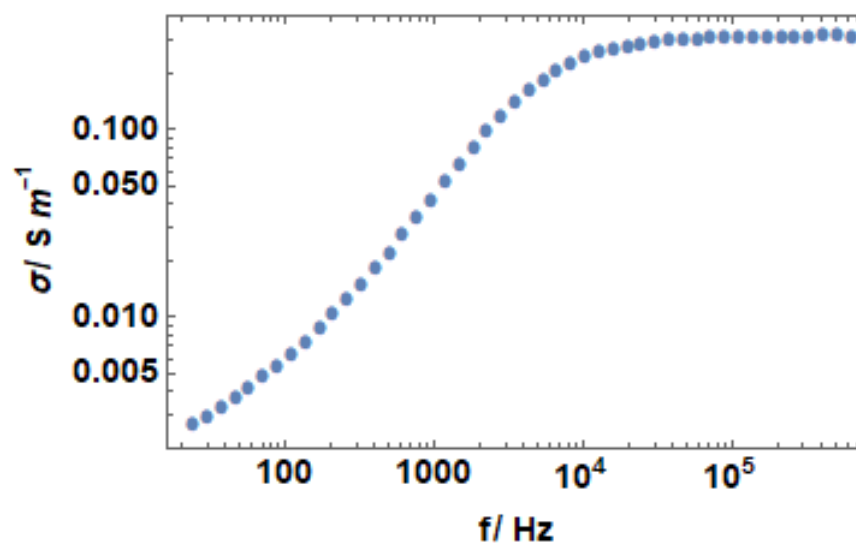


Figure 3. Conductivity vs. frequency.

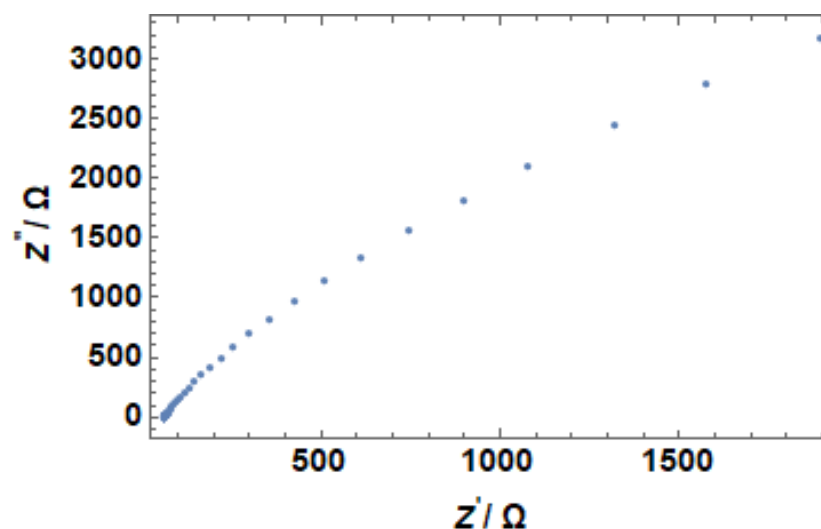


Figure 4. Nyquist plot of $C_4C_1Im BF_4$.

Finally, the conductivity at room temperature measured by GLP31 conductimeter is:

$$\sigma = 0.263 \pm 0.010 \text{ S/m} \quad (11)$$

Obtained values from both apparatus are comparable and are in good concordance with the results of Harris et al. [13] and Rilo et al. [14] After this work, the main conclusion when comparing both techniques could be that conventional conductimeter give us quicker values although RLC provides more reliable results.

6. Conclusions

The identification of the conductive regime, and the conductivity calculation through a least squares fitting, or by averaging of the conductivities in the mentioned regime, gives better results than a traditional conductimeter using a single frequency. Even more, the reproducibility of the impedance spectroscopic is higher than the conductimeter's due to the higher amount of data used to obtain the conductivity. The difference between the conductivity measured by the GLP31 and the RLC could be due to the fact the RLC takes an average value for the conductivity at different frequencies, while the GLP31 measures it at just one.

Author Contributions: Conceptualization, P.V., J.S., and L.M.V.; methodology and data, P.V., J.J.P., F.S., A.M.; software, P.V., F.S., A.M. and L.M.V. writing—original draft preparation, P.V., J.J.P., J.S., M.V., O.C. and L.M.V.; funding acquisition, L.M.V., O.C., J.S. and M.V. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Spanish Ministry of Economy and Competitiveness and FEDER Program through the project MAT2017-89239-C2-1-P and by Xunta de Galicia through GRC ED431C 2020/10 project and the Galician Network of Ionic Liquids (ReGaLIs) ED431D 2017/06. P. Vallet and J. J. Parajó thank funding support of FPI Program from Spanish Ministry of Science, Education and Universities and I2C postdoctoral Program of Xunta de Galicia, respectively.

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